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2-[(Isopropoxycarbonothioyl)sulfanyl]-acetic acid

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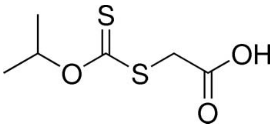
Key indicators: single-crystal X-ray study; *T* = 150 K; mean σ(C–C) = 0.004 Å; *R* factor = 0.046; *wR* factor = 0.095; data-to-parameter ratio = 19.8.

The title compound, $C_6H_{10}O_3S_2$, features a planar C atom connected to one O and two S atoms, the C—S single bond being distinctly longer than the C–S double bond. Two molecules are linked by an O—H···O hydrogen bond about a center of inversion, generating a dimer.

Related literature

For general background to the synthesis and applications of the title compound, see: Stenzel *et al.* (2003); Moad *et al.* (2005, 2008). For applications in polymerization, see: Coote & Radom (2004); Favier *et al.* (2004).



Experimental

Crystal data

$C_6H_{10}O_3S_2$	V = 922.0 (4) Å^3
M_r = 194.26	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 5.0092 (14) Å	μ = 0.54 mm^{-1}
b = 7.712 (2) Å	T = 150 K
c = 23.868 (7) Å	0.05 × 0.02 × 0.02 mm
β = 90.294 (9)°	

Data collection

Bruker APEXII CCD diffractometer	6469 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	2040 independent reflections
$T_{\min}$ = 0.972, $T_{\max}$ = 0.992	1306 reflections with $I > 2\sigma(I)$
	R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046	103 parameters
$wR(F^2)$ = 0.095	H-atom parameters constrained
S = 1.03	$\Delta\rho_{\max}$ = 0.34 e Å^{-3}
2040 reflections	$\Delta\rho_{\min}$ = −0.30 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O3^{i}	0.84	1.83	2.664 (3)	174

Symmetry code: (i) $-x+2, -y, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5039).

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supporting information

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2-[(Isopropoxycarbonothioyl)sulfanyl]acetic acid

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S1. Comment

In reversible addition-fragmentation chain-transfer (RAFT) polymerization, xanthates are used as chain transfer agents (CTA) for reversible-deactivation radical polymerization (RDRP) of vinyl acetate (Moad *et al.*, 2005, 2008). Vinyl acetate is one of the typical monomers that cannot be easily polymerized in RDRP, because vinyl acetate radicals are highly unstable. However, xanthates destabilize the intermediate radicals in the RAFT equilibriums, and RDRP can be achieved (Coote & Radom, 2004; Favier *et al.*, 2004). Stenzel *et al.* (2003) synthesized 2-(isopropoxycarbonothioylthio)acetate as the CTA to mediate the polymerization of vinyl acetate, but lack of functionality limits its applications. Therefore, 2-(isopropoxycarbonothioylthio)acetic acid was synthesized. It was employed in RAFT polymerization of vinyl acetate, with poly(vinyl acetate) having carboxylic acid end groups successfully obtained.

Investigation of the single-crystal of 2-(isopropoxycarbonothioylthio)acetic acid was conducted to understand its structural properties.

S2. Experimental

Potassium hydroxide 5.6 g (50 mmol) and 2-propanol 100 ml were mixed to form a homogeneous solution, after which carbon disulfide 20 ml was added dropwise at room temperature. The mixture was kept stirred for 1 day at 40 °C. Then the solvent and residual carbon disulfide were evaporated to obtrain a light yellow powder. The powder was dissolved in methanol, and mixed with the methanol solution of bromoacetic acid. The reaction was conducted at 40 °C for 20 h. Salts were filtered out and solvents were evaporated. The oil was washed with excess diluted hydrochloric acid and extracted with ethyl ether. The crude product was run through a silica gel column with a solvent mixture of ethyl ether/hexanes (1:2). Colorless crystals of 2-(isopropoxycarbonothioylthio)acetic acid were obtained from recrystalization in hexanes. m.p. 44.3°C (DSC). MS: 194.0078.

S3. Refinement

The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon/oxygen atoms.

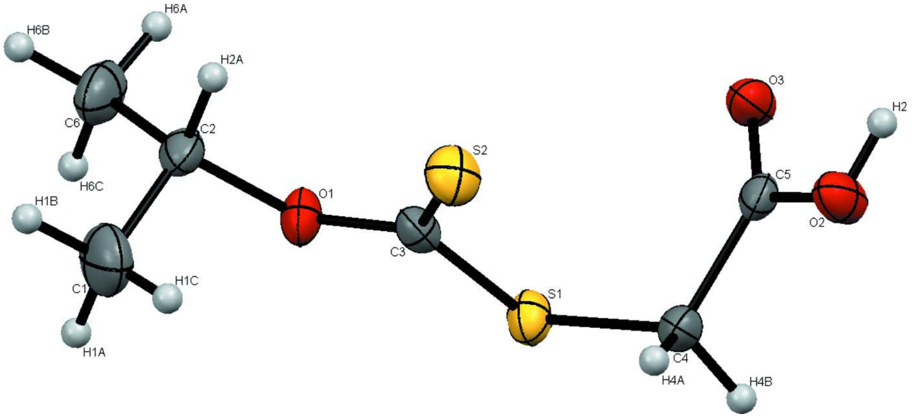

Figure 1

View of the title compound (50% probability displacement ellipsoids).

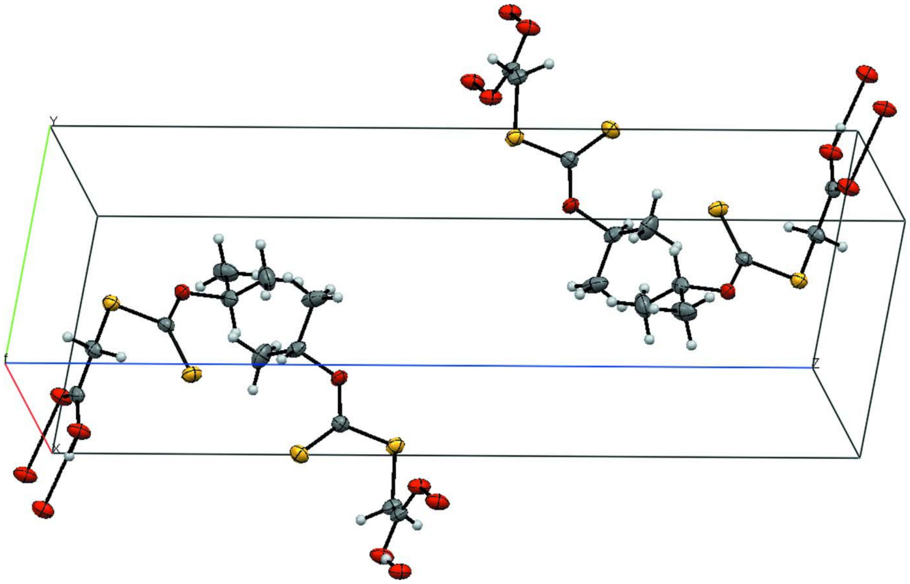

Figure 2

Packing diagram of the structure with H-bonds.

2-[(Isopropoxycarbonothioyl)sulfanyl]acetic acid

Crystal data

$C_6H_{10}O_3S_2$
$M_r = 194.26$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 5.0092$ (14) Å
$b = 7.712$ (2) Å
$c = 23.868$ (7) Å
$\beta = 90.294$ (9)°
$V = 922.0$ (4) Å^3
$Z = 4$

$F(000) = 408$
$D_x = 1.399$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 981 reflections
$\theta = 2.8$–23.5°
$\mu = 0.54$ mm^{-1}
$T = 150$ K
Block, colourless
0.05 × 0.02 × 0.02 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{\min} = 0.972$, $T_{\max} = 0.992$

6469 measured reflections
2040 independent reflections
1306 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.061$
$\theta_{\max} = 27.1°$, $\theta_{\min} = 1.7°$
$h = -3 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.095$
$S = 1.03$
2040 reflections
103 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.0157P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
S1	0.62574 (14)	0.49105 (9)	0.06736 (3)	0.0265 (2)
S2	0.97062 (15)	0.32368 (10)	0.15640 (3)	0.0302 (2)
O1	0.9373 (4)	0.6573 (2)	0.12779 (8)	0.0252 (5)
O2	0.7271 (4)	−0.0108 (2)	0.04984 (9)	0.0311 (5)
H2	0.8469	−0.0692	0.0341	0.047*
O3	0.9230 (4)	0.2085 (2)	0.00436 (8)	0.0288 (5)
C1	0.9765 (7)	0.7333 (4)	0.22585 (13)	0.0456 (9)
H1A	0.8459	0.8265	0.2205	0.068*
H1B	1.1010	0.7651	0.2559	0.068*
H1C	0.8835	0.6260	0.2359	0.068*
C2	1.1292 (5)	0.7057 (4)	0.17223 (12)	0.0267 (7)
H2A	1.2634	0.6110	0.1775	0.032*
C3	0.8641 (5)	0.4925 (3)	0.12137 (11)	0.0223 (6)
C4	0.5442 (5)	0.2657 (3)	0.06314 (12)	0.0246 (7)
H4A	0.5113	0.2220	0.1015	0.030*
H4B	0.3758	0.2532	0.0416	0.030*

C5	0.7540 (5)	0.1537 (4)	0.03631 (11)	0.0226 (6)
C6	1.2649 (6)	0.8665 (4)	0.15058 (15)	0.0408 (9)
H6A	1.3543	0.8400	0.1152	0.061*
H6B	1.3971	0.9064	0.1781	0.061*
H6C	1.1315	0.9576	0.1444	0.061*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0297 (4)	0.0200 (4)	0.0297 (4)	0.0018 (3)	−0.0059 (3)	−0.0032 (4)
S2	0.0362 (4)	0.0214 (4)	0.0330 (4)	0.0034 (3)	−0.0032 (3)	0.0049 (4)
O1	0.0320 (11)	0.0181 (11)	0.0255 (11)	−0.0002 (8)	−0.0079 (9)	−0.0033 (9)
O2	0.0313 (11)	0.0196 (11)	0.0426 (13)	−0.0001 (9)	0.0099 (10)	−0.0015 (11)
O3	0.0268 (11)	0.0223 (11)	0.0375 (12)	−0.0038 (9)	0.0091 (10)	−0.0040 (10)
C1	0.052 (2)	0.052 (2)	0.0323 (19)	−0.0011 (18)	−0.0065 (18)	−0.0151 (18)
C2	0.0212 (14)	0.0253 (16)	0.0334 (17)	0.0003 (13)	−0.0074 (13)	−0.0061 (15)
C3	0.0252 (14)	0.0200 (14)	0.0218 (15)	0.0024 (13)	0.0043 (12)	−0.0025 (14)
C4	0.0203 (15)	0.0236 (16)	0.0299 (16)	−0.0029 (12)	0.0013 (13)	−0.0061 (13)
C5	0.0201 (14)	0.0205 (16)	0.0270 (16)	−0.0027 (12)	−0.0053 (13)	−0.0052 (14)
C6	0.0362 (18)	0.0232 (17)	0.063 (2)	−0.0052 (14)	−0.0075 (17)	−0.0075 (18)

Geometric parameters (Å, º)

S1—C3	1.753 (3)	C1—H1B	0.9800
S1—C4	1.788 (3)	C1—H1C	0.9800
S2—C3	1.635 (3)	C2—C6	1.506 (4)
O1—C3	1.331 (3)	C2—H2A	1.0000
O1—C2	1.476 (3)	C4—C5	1.506 (4)
O2—C5	1.316 (3)	C4—H4A	0.9900
O2—H2	0.8400	C4—H4B	0.9900
O3—C5	1.218 (3)	C6—H6A	0.9800
C1—C2	1.509 (4)	C6—H6B	0.9800
C1—H1A	0.9800	C6—H6C	0.9800

C3—S1—C4	101.66 (13)	S2—C3—S1	126.18 (17)
C3—O1—C2	120.2 (2)	C5—C4—S1	114.94 (19)
C5—O2—H2	109.5	C5—C4—H4A	108.5
C2—C1—H1A	109.5	S1—C4—H4A	108.5
C2—C1—H1B	109.5	C5—C4—H4B	108.5
H1A—C1—H1B	109.5	S1—C4—H4B	108.5
C2—C1—H1C	109.5	H4A—C4—H4B	107.5
H1A—C1—H1C	109.5	O3—C5—O2	124.1 (3)
H1B—C1—H1C	109.5	O3—C5—C4	123.8 (3)
O1—C2—C6	104.8 (2)	O2—C5—C4	112.1 (2)
O1—C2—C1	108.3 (2)	C2—C6—H6A	109.5
C6—C2—C1	114.0 (3)	C2—C6—H6B	109.5
O1—C2—H2A	109.9	H6A—C6—H6B	109.5
C6—C2—H2A	109.9	C2—C6—H6C	109.5

C1—C2—H2A	109.9	H6A—C6—H6C	109.5
O1—C3—S2	127.8 (2)	H6B—C6—H6C	109.5
O1—C3—S1	106.06 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3^{i}	0.84	1.83	2.664 (3)	174

Symmetry code: (i) −*x*+2, −*y*, −*z*.